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Description

This invention relates to a flexible composite material useful for the molding of composite articles, and to a process for preparing the material.

A well known composite material containing reinforcing fibers eg carbon fibers is a prepreg in the form of a tape or a woven cloth formed by coating a solution of a thermosetting resin or a low-viscosity molten thermosetting resin on a tow or a woven cloth of the reinforcing fibers or covering the tow or the woven cloth with the solution or the low-viscosity molten material. Such a prepreg is extremely high in adhesion and poor in flexibility so that it has problems with handling and post-processing. A tape of a carbon fiber-containing thermoplastic resin prepared by extruding a carbon fiber tape in which a thermoplastic resin having a high melting point is impregnated is also known; however, such a carbon fiber-containing thermoplastic resin tape is in the state of an extremely rigid board so that it may cause difficulties in the formation of woven clothes and moreover it cannot be subjected to drape forming through molds with complex shapes.

In order to overcome drawbacks as described above, there has recently been proposed a continuous fiber tow (European Publication No. 156599A and No. 156600A) which is formed from a tight blend of about 90 % to 30 % by volume of spun fibers of a thermoplastic polymer and about 10 % to 70 % by volume of carbon fibers or non-thermoplastic reinforcing fibers, each based on the total fiber content; and a flexible composite material (European Publication No. 133825A) which is formed by covering coarse fiber filaments impregnated by a thermoplastic resin powder with a flexible covering material. These composite materials are more suitable for drape forming through molds with complex shapes in terms of flexibility, as compared to known carbon fiber-containing thermoplatic resin tape; however, they still have drawbacks as will now be described.

The continuous fiber tow, on the one hand, may have fuzzes on its surface so that the step of weaving cloth from it is hampered. It also leads to the formation of a large number of fuzzes on the resulting woven cloth, thereby making it difficult to provide woven cloths of practical value. Furthermore, as carbon fibers are exposed on the surface of the composite material, the fibers are easily damaged during the handling and become fuzzed. Moreover, the composite material has an additional disadvantage that the properties of molded products formed from it are caused to be impaired because the thermoplastic resin fibers and the carbon fibers used are exposed in the atmosphere so that air and moisture can permeate through the spaces among the fibers.

The flexible composite material of EP-A-133825, on the other hand, involves the difficulty of properly determining the blend ratios of the reinforcing fibers and the thermoplastic resin powders because the thermoplastic resin powders are caused to adhere to coarse fiber filaments (reinforcing fibers) using a fluidized layer and so on, so that the properties of the resulting molded products are not rendered uniform. This causes the problem that the material properties are unstable. In instances where the composite material is employed in the form of shortly cut chips or where it is woven into cloth in such a form, there is the difficulty that the resin powders in the sleeve will be caused to be scattered during cutting so that the quantitative and uniform properties as a composite material may be impaired and the working environment will be caused to be worsened. Further, in the production of the composite material, an extremely severe step of producing powdery particles is required so as to define average particle sizes of the powdery particles within a particular range to maintain a stably fluidized state of the fluidized layer. This increases the cost of production. As coarse fiber filaments are used it is hard to tightly bond the coarse fiber filaments to the flexible covering material, leading to the ready permeation into the composite material of air that may cause a decrease in the material properties of the resultant molded products. There is also the problem that the removal of air from the sleeve is difficult because this will cause the powdery particles to migrate, thus adversely influencing the quantitative and uniform properties of the resultant molded products.

GB-A-1290781 (and its French counterpart FR-A-2028162) discloses a plastics coated thread for use in making a sieve or screen of a paper-making machine, and which comprises a multifilament core which is coated with a thermoplastic resin. It is stated that the filaments of the core "may consist of untreated or treated, for example provided with a thin coating, synthetic fibers, eg polyester fibres, or of artificial fibres or natural fibres, or inorganic fibres, eg glass fibre, or of a mixture of such fibres.".

The present invention has the object to provide a novel flexible composite material that can permit blending of reinforcing fibers and thermoplastic resin fibers in the production of the composite material at a quantitative and uniform rate, and which can be processed in an extremely favorable manner, leading to the formation of molded articles with superior mechanical properties such as tensile strength, bending strength and so on. The present invention also aims to provide a process for preparing the flexible composite material in an industrially

favorable manner.

In accordance with one aspect of the present invention, therefore, there is provided a flexible composite material comprising a core (1) composed of a substantially uniformly distributed blend of thermoplastic resin fibers (3) and reinforcing fibers (4), and a flexible sleeve (2) formed of a thermoplastic resin and surrounding said core (1), said thermoplastic resin fibers (3) melting at a temperature at which said reinforcing fibers (4) remain solid and having a denier number not greater than 3.

In another aspect, the present invention provides a process for preparing a flexible composite material, comprising the steps of:

(a) providing thermoplastic resin fibers (3) and reinforcing fibers (4), said thermoplastic resin fibers (3) melting at a temperature at which said reinforcing fibers (4) remain solid and having a denier number not greater than 3;

(b) intimately blending said thermoplastic resin fibers (3) and reinforcing fibers (4);

(c) assembling said blended fibers to obtain a core (1); and

(d) extruding a thermoplastic resin over said core (1) to form a sleeve (2) surrounding said core (1).

The flexible composite material according to the present invention permits the blending ratio of the reinforcing fibers and the thermoplastic resin fibers to be determined freely and quantitatively, unlike in the case that a thermoplastic resin in the form of powder is employed, because the blend is used as the core material and a flexible sleeve made from a thermoplastic resin is provided around the core material. As the resultant blended fiber bundle is superior in flexibility, quality and uniformity, the flexible composite material according to the present invention can provide molded articles with superior mechanical properties such as a tensile strength, bending strength and so on.

Also the flexible composite material according to the present invention is provided with a flexible sleeve made from the thermoplastic resin around the core material, as described above, so that air or moisture are prevented from permeating into the flexible composite material, thereby enabling a remarkable improvement in the mechanical properties of the resulting molded articles. The flexible composite material does not cause fuzzing on the surface thereof and no reinforcing fibers are exposed thereon, so that a cloth weaving step and handling are rendered easy, thus causing no damage to the reinforcing fibers in the resulting clothes, woven clothes and so on, and leading to extremely good post-processing. These remarkable results follow from the construction of the flexible composite material, ie with a core composed of a blend of reinforcing and thermoplastic resin fibers surrounded by a flexible thermoplastic sleeve.

On the other hand, in instances where a thermoplastic resin in the form of powders is employed in the place of the thermoplastic resin fiber, it is difficult to quantitate a rate of blending of the reinforcing fibers and thermoplastic resin fibers, so that a composite material of high quality and uniformity cannot then be produced. When such composite material is cut, the powders within it are caused to be removed so that the quantitative property is further impaired, thus leading to a worsening of the working environment and a rise of production costs.

In instances where the bundle of reinforcing fibers and thermoplastic resin fibers is not surrounded with a sleeve, the blended fiber bundle is caused to be exposed directly to air so that air permeates into spaces among the fibers and the properties of resultant molded articles are inferior, leading to the production of unstable and non-uniform molded articles. Further, since such composite materials may cause a remarkable number of fuzzes and then the reinforcing fiber is caused to be exposed on the surface, the post- processability can become extremely poor.

The present invention will now be described in more detail with reference to the accompanying drawings, in which:

Fig. 1 is a fragmentary, perspective view, cut away in part, schematically showing a flexible composite material according to the present invention; and

Fig. 2 is a diagrammatic illustration of an apparatus suitable for the preparation of the composite material of the present invention.

Referring to Fig. 1, the reference numeral 1 designates a blended fiber bundle or core surrounded by a flexible thermoplastic resin sleeve 2. The blended fiber core 1 is composed of thermoplastic resin fibers 3 and reinforcing fibers 4. The filaments of the two fibers 3 and 4 are each generally continuous and are substantially uniformly distributed in the plane perpendicular to the axis of the core 1.

The amount of the thermoplastic resin fibers 3 and the reinforcing fibers 4 in the core may vary with the purpose of or the manner of using the flexible composite material, and may preferably range from about 1 % to about 89 % by volume and from about 99 % to about 11 % by volume, respectively, based on the total fiber content. If the blending ratios of the thermpolastic resin fibers 3 to the reinforcing fibers 4 are below this range, it can become difficult to produce molded articles with high quality and uniformity. If the blending ratio exceeds the above range, the reinforcing effect created by the reinforcing fibers may be insuffi-

cient. More preferably, the amount of the thermoplastic resin fibers 3 is from about 15% to about 30% and the amount of the reinforcing fibers 4 is from about 85% to about 70%, each based on the total fiber content.

The thickness of the flexible sleeve 2 made from the thermoplastic resin may range preferably from about 5 to about 2,000 µm and, more preferably, from about 10 to about 200 µm. A thickness below about 5 µm can make it difficult to form a uniform sleeve, but on the other hand, if it exceeds about 2,000 µm, the flexibility of the composite material may be insufficient.

In the flexible composite material according to the present invention, the denier numbers of the filaments of the thermoplastic resin fibers must not be greater than 3 and preferably is not greater than 1, per each filament. Although the number of the filaments may conveniently vary with the denier numbers of the filaments, it may range generally from about 5 to about 20,000,000 and, more preferably, from about 10 to about 100,000.

The reinforcing fibers to be used for the present invention suitably have a filament denier number ranging from about 0.05 to about 600 and the number of filaments ranges from about 50 to about 300,000 and preferably have a filament denier number ranging from about 0.25 to about 16, with the number of filaments ranging from about 100 to about 48,000.

The diameters of the thermoplastic resin fibers to be used for the present invention may range generally from about 0.5 to about 60 µm and preferably from about 2 to 11 µm, while the diameters of the reinforcing fibers may range generally from about 3 to about 50 µm and preferably from about 6 to about 30 µm. It is preferred to generally use thermoplastic resin fibers having a filament size smaller than that of the reinforcing fibers, because the thinner the thermoplastic resin fiber filaments, the greater becomes the number of the filaments and, thus, the uniformity of the fiber blend is improved.

The flexible composite material according to the present invention is superior in mechanical strength when molded in articles because air and moisture are unlikely to permeate thereinto because the blended fiber bundle 1 composed of the thermoplastic resin fibers 3 and the reinforcing fibers 4 is used as a core material and a flexible sleeve 2 made from the thermoplastic resin is provided over the surface of the core material 1, as described above.

In accordance with the present invention, the blended fiber bundle 1 and the sleeve 2 can be closely bonded to each other when the step of covering the core with the sleeve is performed while keeping the core under vacuum using a dealring pump, as described hereinafter, so that molded articles having superior mechanical strength can be produced. Such a flexible composite material in which the blended filaments bundle 1 is closely bonded to the sleeve 2 is particularly suitable for a filament winding molding material as will be described below and is molded into articles requiring high quality. In the composite material according to the present invention, it may be possible to provide an arbitrary number of annular knots or depressions thereon using a stamping or hot pressing device in order to maintain the close bonding between the sleeve 2 and the blended fiber bundle 1. The composite material of this shape is advantageous, for example, in instances where it is to be subsequently cut into chips between each adjacent knots.

The thermoplastic resin fibers to be used for the present invention may be formed of polymers such as polyamides, polyesters, polyethylenes, polypropylenes, polyvinylidene fluorides, polamideimides, polyimides, polyetherimides, polyethersulfones and polyetheretherketones. More specifically, the polyamide may include homopolymers or copolymers such as nylon 66, nylon 6, nylon 12 and nylon 6/66/12 terpolymer. The polyester may include homopolymers or copolymers such as polyethylene terephthalate, polybutylene terephthalate, polyethylene-2,6-naphthalate, polyoxyethoxybenzoate and aromatic polyester.

As the reinforcing fibers 4 to be used for the present invention may be employed carbon fibers, glass fibers or polyamide fibers. More specifically, the carbon fibers may be divided basically into two groups according to the difference in the raw material to be used. A first group are those prepared by carbonizing petroleum pitch or coal tar pitch used as raw materials. The second group are those prepared by carbonizing natural or synthetic fibers used as raw materials. Any one of these groups may be employed for the present invention. In instances where pitch is employed as a raw material, the pitch is prepared so as to be in a state suitable for spinning and is then converted into fibers, followed by being subjected to infusion and carbonization. For example, pitch prepared to have softening points ranging from 180 to 300 °C is molten spun at temperatures from 250 to 350 °C, then subjected to infusion at temperatures from 150 to 300 °C using an oxidizing gas and carbonized at temperatures from 800 to 2,500 °C. In instances where fibers are used as raw materials, cellulose or acrylic fibers, particularly acrylonitrile copolymer fibers, are suitably used as raw materials. They are subjected to a heat treatment and then carbonized. Particularly suitable for the present invention are carbon fibers prepared from pitch.

The thermoplastic resins to be used for forming the flexible sleeve 2 according to the present invention may include a polymer such as polyamide, polyester, polyethylene, polypropylene, polyvinylidene fluoride, polyamidimide, polyimide, polyether imide, polyether sulphone or polyetheretherketone. More specifically, the polyamides may include a homopolymer or copolymer such as nylon 66, nylone 6, nylon 12, and nylon 6/66/12 terpolymer. The specific polyesters may include polyethylene terephthalate, polybutylene terephthalate, polyethylene-2,6-naphthalate, polyoxyethoxybenzoate or aromatic polyester. The melting points of the thermoplastic resins to be used as the sleeve-forming material are preferably equal to or lower than those of the thermoplastic resin fibers 3.

A preferred process for the preparation of the flexible composite material will now be described. The process essentially comprises the steps of blending a thermoplastic resin fiber bundle and a reinforcing fiber bundle and then covering the resultant blended fibers with a thermoplastic resin so as to form a sleeve around the blended fiber bundle.

Referring now to Fig. 2, a bundle of a reinforcing fiber 11 and a bundle of a thermoplastic resin fiber 12 wound on bobbins (not shown) are continuously drawn at a constant speed by a Nelson type feed roller 14 through a fiber blending device 13. The fiber blending device 13 may be of any conventional type and is not specifically shown herein. Briefly, the device 13 is composed of air nozzles and an intermixing means. Designated as 23 and 24 is unwinding equipment for controlling the feed of the fibers.

The two different fiber bundles supplied to the blending device 13 are uniformly spread or separated by the aid of dry air blown from the nozzles and then caused to go into contact with each other for intermixing. During the blending, a tension of 2 grams or higher, for example, is arranged to be applied to the fibers 11 and 12. The blended fiber bundle obtained in the blending device 13 is transferred to a sleeve-covering device composed of a thermoplastic resin extruder 18 and a sleeve-covering cross bed 16, and is covered there with the flexible thermoplastic resin supplied to the extruder 18.

The composite material now provided with the sleeve is then cooled and solidified by a cooling device 20, followed by drawing at a constant speed by means of a Nelson type feed roller 21 and winding by means of a take-up device 22. The reference numerals 15 and 25 denote sizing rollers which are preferably disposed for surface-treating the reinforcing fiber bundle and the blended fiber bundle, respectively, for the purpose of preventing fuzzes from being caused on the bundles and of increasing the tension of the bundles. The sizing agent to be used for the sizing may also serve to function as a converging agent during the formation of the composite material and also as a binder between the reinforcing fiber and the thermoplastic resin fiber during the molding of the composite material.

In accordance with the present invention, in instances where the sizing rollers 15 and 25 are employed, the production efficiency can be increased to a considerable extent and there can be produced a blended fiber bundle in which the thermoplastic resin fibers are closely bonded to the reinforcing fibers and also molded articles in which the thermoplastic resin is closely bonded to the reinforcing fiber.

In Fig. 2, the reference numeral 17 designates a deairing pump, which is useful for the production of composite material in which the core 1 (Fig. 1) of the blended filaments bundle is in close contact with the thermoplastic resin sleeve 2 (Fig. 1) and, hence, for the production of molded articles having an extremely small porosity. That is, by connecting the pump 17 to the cross bed 16, the blended fiber bundle is maintained under vacuum so that interstices between the blended fibers and between the fibers and the sleeve may be reduced to provide tight bonding between the fibers and between the core and the sleeve.

Designated as 19 is a stamping or knot forming device, which is useful for the production of the composite material according to the present invention suitable for being cut into a multiplicity of chips. The stamping device 19 can form a plurality of axially spaced apart annular depressed portions or grooves on the outer periphery of the sleeve by radially inwardly pressing, with heating, the composite material drawn from the sleeve forming step, whereby the sleeve and the fibers are tightened together at the pressed portions. As a result, when the composite material is cut into chips at positions other than the pressed portions, the cut fibers are prevented from separating from each other or from the sleeve and remain bound together. In accordance with the present invention, in addition to the blending device described above, various other types of fiber blending device conventionally used may be conveniently employed, for example, an air processor or the like.

The composite material according to the present invention may be used as a filament winding material or as a pressurized molding material. In the case of filament winding, the composite material according to the present invention is wound on a mandrel or a former, caused to be heated under pressure at temperatures higher than that of the thermoplastic resins by heating means

so as to melt or fuse the thermoplastic resin of the sleeve and the thermoplastic fibers, and then resolidified. Thereafter the mandrels and formers are then removed or they may become part of the molded products. In the case of pressurized molding, the composite material may be placed on a mold, heated at temperatures higher than the melting point of the thermoplastic resin under pressure to melt the thermoplastic resin and the reinforcing fibers integrally thereto, and then resolidified.

By using the composite material according to the present invention, there may be produced a solid molded article in which the reinforcing fibers are dispersed to a sufficient degree. It permits the ready production of products of complex dimensional shapes and of a small radius of curvature.

The composite material according to the present invention may be molded by molding means such as the filament winding method and the pressurized molding method into structural parts for automobiles, tennis racket frames, hockey sticks, skiing stocks, fishing rods, golf club shaft and so on. Furthermore, the composite material in the fiber form according to the present invention may be molded into mats in combination with other fibers by means of conventional weaving method.

The flexible composite material according to the present invention may be prepared by blending the thermoplastic resin fibers and the reinforcing fibers in arbitrary and quantitative blending ratios because, as described above, the blended fiber bundle composed of the thermoplastic resin fibers and the reinforcing fibers are used as a core material and a flexible sleeve made from the thermoplastic resin is provided around the core material. It further is practically valuable because it is superior in post-processibility and flexibility, whereby molded articles with extremely high tensile strength and bending strength characteristics can be obtained. The process for the preparation of the flexible composite material according to the present invention is also industrially favorable because it has relatively few steps and it only requires the use of a simple apparatus.

The following examples will further illustrate the present invention.

Example 1

Both a bundle of nylon 66 filaments as well as pellets of the same polymer were prepared using a polymer prepared from hexamethylene diamine/adipic acid (HA salt) as a base material. The density of this nylon 66 was 1.14 g/cc, and the bundle was composed of 600 filaments of 3 denier each. Its tensile strength was 6.4 kg/mm^2, and the elongation was 38 %. The reinforcing fibers to be blended with the nylon 66 fibers was a bundle of carbon fibers made from petroleum pitch. The carbon fiber bundle was composed of 6,000 filaments and had a density of 1.71 g/cc, a tensile strength of 310 kg/mm^2 , a tensile elastic modulas of 22 x 10^3 kg/mm^2 , and an elongation of 1.4 %. A flexible composite material was made from these fibers having apparatus such as shown in Fig. 2. Thus, the carbon bundle and the nylon 66 bundle wound on bobbins were continuosly drawn through the fiber blending device 13 by the Nelson type feed roller 14 at a constant speed to obtain a blended fiber bundle composed of 64 % by volume of the carbon fiber and 36 % by volume of the nylon 66 fiber.

The fiber blending device 13 was composed of air nozzles and a fiber intermixing means. The two fibers supplied were each spread by blowing dry air from the nozzles, and both the spread fibers were passed through two small long fixed plates arranged in parallel with each other in the up-and-down positions to effect intermixing of the two fibers. During this step, a tension of about 30 grams was applied to the fibers using a sensor.

The blended fiber bundle thus formed was then transferred to a sleeve-covering device composed of the thermoplastic resin extruder 18 and a sleeve-covering cross head 16. During this step, the pellets of nylon 66 prepared as described above were supplied to the extruder 18 so as to form a sleeve around the blended fiber bundle, the product was then cooled by means of the cooling device 20 to be solidified, the product was drawn at a constant velocity by means of the Nelson type feed roller 11, and then it was wound by the winding apparatus 22. The extruder 18 was arranged to have a screw diameter of 20 mm and an extruding velocity of 0.34 liter/hour, and the temperature of the cross head die was set to be 281 °C and the drawing velocity was 10 m/minute.

The resulting sleeve surrounding the blended fiber bundle had an inner diameter of 5 mm, a thickness of 36 µm and a volume of 47% based on of the volume of the carbon fiber. The resultant composite material was woven using a rapier loom to give a plain woven cloth of high quality without any fuzz caused and carbon fibers exposed on the surface thereof.

The composite material was also tightly wound to a thickness of about 6 mm on an aluminum alloy plate having a width of 200 mm and a thickness of 5 mm and then placed into a mold of a pressure molding apparatus. The mold was heated to 280 °C and kept for 5 minutes, and then given a pressure of 32 kg/cm^2 for 20 minutes. The mold was then cooled to ambient temperature while the pressure was kept applied. The resultant molded product was removed from the mold and cut into test pieces of 175 mm x 20 mm x 3 mm and 80

mm x 25 mm x 3 mm, respectively, so as to allow the carbon fibers to be positioned in the lengthwise direction. Using each 20 test pieces, the tensile and the bending tests were conducted. The average tensile strength for 20 test pieces was found to be 105.7 kg/mm^2 and the bending velocity was 91.4 kg/mm^2.

Example 2

Test pieces were prepared by following Example 1 with the exception that the number of nylon 66 fiber filaments was 3,400 and the denier number per filament was 0.5. The test results were: tensile strength of 149.6 kg/mm^2 and bending strength of 131.3 kg/mm^2. These figures are higher than those obtained in Example 1, and they show that a more uniform composite material resulted from the reduction in the denier number of the nylon 66 filaments.

Example 3

A blended fiber bundle composed of 74 % by volume of carbon fiber and 26 % by volume of nylon 66 fiber was prepared by following Example 1 with the exception that the number of nylon 66 fiber filaments was changed to 370 and the denier number per filament was changed to 0.5. Using this blended filaments bundle, a composite material was prepared in the same manner as in Example 1 and test pieces were likewise prepared and tested. The tensile strength was found to be 120.8 kg/mm^2 and the bending strength was 112.2 kg/mm^2. The composite material was found to contain carbon fibers in higher content than that obtained in Example 1 and be superior to that of Example 1.

Example 4

A composite material was prepared in substantially the same manner as in Example 1 with the exception that the sleeve forming step was performed using the deairing pump 17 so as to closely bind the blended fiber bundle composed of the nylon 66 fibers and the carbon fibers. Test pieces were then likewise produced, and their tensile strength was found to be 138.4 kg/mm^2 and the bending strength of 130.1 kg/mm^2. This shows that the porosity of the molded product was reduced.

Example 5

A composite material was prepared by following Example 1 with the exception that the tension before and after the fiber blending device 13 was changed to about 75 grams. This made it possible to set the extruding velocity at 2.04 liters/hour and the final drawing velocity at 60 meters/minute, leading to a remarkable increase in productivity. The tensile strength was found to be 104.9 kg/mm^2 and the bending strength was 91.8 kg/mm^2.

Example 6

A composite material was prepared by following Example 1 with the exception that the carbon fiber bundle was surface treated by the sizing roller 25 and the blended fiber bundle by the sizing roller 15, and the tension before and after the fiber blending device was changed to about 50 grams. This permitted the extruding velocity to be set at 2.72 liters/hour and the final drawing velocity at 80 meters/minute, leading to a remarkable increase in production speed. The tensile strength was found to be 109.2 kg/mm^2 and the bending strength was 90.3 kg/mm^2.

Example 7

A composite material was prepared in substantially the same manner as in Example 1 with the exception that the sleeve was closely bonded to the blended fiber bundle composed of the nylon 66 fibers and the carbon fibers in which the sleeve forming step was performed under a reduced pressure using the deairing pump 17, and the composite material was provided along its length with knots (annular grooves) at 10 mm spacing by stamping at a temperature of about 280 °C and a pressure of about 70 Kg/cm^2 by means of the stamping device 19. The resulting composite material was chopped into lengths of 50 mm. Substantially no separation of fibers from the sleeve was observed. The chopped material was dispersed in radom directions and laminated to give a composite material in the felt state having a thickness of 4.2 mm. This was heated at 270 °C using a far infrared heater and then inserted into a press mold that was operated under the pressure of 60 kg/cm^2, leading to the production of composite products having a variety of curved surfaces.

Comparative Example 1

The blended fiber bundle prepared by the process of Example 1 was wound directly without passage through the sleeve covering device. This was subjected to plain weaving with a rapier loom, resulting in a woven cloth with a remarkable degree of fuzzes caused on the surface, and the cloth was found inpractical. Test pieces were prepared in substantially the same manner as in Example 1 and subjected to tests. The results were: tensile strength of 74.2 kg/mm^2 and bending strength of 63.1 kg/mm^2.

Claims

1. A flexible composite material comprising a core (1) composed of a substantially uniformly distributed blend of thermoplastic resin fibers (3) and reinforcing fibers (4), and a flexible sleeve (2) formed of a thermoplastic resin and surrounding said core (1), said thermoplastic resin fibers (3) melting at a temperature at which said reinforcing fibers (4) remain solid and having a denier number not greater than 3.

2. A flexible composite material according to Claim 1, wherein said blend comprises from 15-30% by volume of the said thermoplastic resin fibers (3) and correspondingly from 85-70% by volume of said reinforcing fibers (4).

3. A flexible component material according to Claim 1 or Claim 2, wherein said thermoplastic resin fibers (3) have a filament denier number not greater than 1.

4. A flexible composite material according to Claim 3, wherein said reinforcing fibers (3) have a filament denier number in the range of 0.25 to 1.

5. A flexible composite material according to any preceding claim, wherein said sleeve (2) has a thickness in the range of from 10 to 200 µm.

6. A flexible composite material according to any preceding claim, wherein said sleeve (2) is in close contact with the entire periphery of said core (1).

7. A flexible composite material according to any preceding claim, and being provided with a plurality of longitudinally equally spaced apart annular pressed portions on the outer periphery of said sleeve (2), each annular pressed portion being formed by radially inwardly hot pressing the periphery of the sleeve (2) so as to tighten the sleeve and the fibers (3,4) together.

8. A flexible composite material according to any preceding claim, wherein said reinforcing fibers are selected from carbon fibers, glass fibers, polyamide fibers and mixtures thereof.

9. A process for preparing a flexible composite material, comprising the steps of:
(a) providing thermoplastic resin fibers (3) and reinforcing fibers (4), said thermoplastic resin fibers (3) melting at a temperature at which said reinforcing fibers (4) remain solid and having a denier number not greater than 3;
(b) intimately blending said thermoplastic resin fibers (3) and reinforcing fibers (4);
(c) assembling said blended fibers to obtain a core (1); and
(d) extruding a thermoplastic resin over said core (1) to form a sleeve (2) surrounding said core (1).

10. A process according to Claim 9, wherein said blending step (b) is carried out while applying a tension of at least about 2 g to each of said thermoplastic resin fibers (3) and said reinforcing fibers (4).

11. A process according to Claim 9 or Claim 10, further comprising treating said reinforcing fibers (4) with a sizing agent before said blending step (b).

12. A process according to any one of Claims 9-11, further comprising treating said core (1) with a sizing agent before said extruding step (d).

13. A process according to any one of Claims 9-12, wherein said extruding step (d) is carried out while maintaining said core (1) under vacuum so as to substantially reduce interstices between the blended fibers (3,4) of said core (1) and between said core (1) and said sleeve (2).

14. A process according to any one of Claims 9-13, further comprising radially inwardly hot-pressing the sleeve (2) after said extruding step (d) to form a plurality of axially equally spaced apart annular depressed portions on the periphery of the sleeve (2) so that the blended fibers (3,4) and the sleeve (2) are tightly bound at each depressed portion.

15. A process according to Claim 14, further comprising cutting into chips the product obtained after said hot-pressing step at positions other than the depressed portions.

Revendications

1. Matériau composite flexible comprenant un noyau (1) composé d'un mélange distribué de façon sensiblement uniforme de fibres (3) en résine thermoplastique et de fibres d'armement (4), et un manchon flexible (2) constitué d'une résine thermoplastique et entourant ledit noyau (1), lesdites fibres (3) en résine thermoplastique fondant à une température à laquelle

lesdites fibres d'armement (4) restent solides et ayant un denier non supérieur à 3.

2. Matériau composite flexible selon la revendication 1, dans lequel ledit mélange comprend de 15 à 30 % en volume desdites fibres (3) en résine thermoplastique et par correspondance de 85 à 70 % en volume desdites fibres d'armement (4).

3. Matériau composite flexible selon la revendication 1 ou la revendication 2, dans lequel lesdites fibres (3) en résine thermoplastique ont un denier des filaments non supérieur à 1.

4. Matériau composite flexible selon la revendication 3, dans lequel lesdites fibres d'armement (3) ont un denier des filaments dans la gamme 0,25 à 1.

5. Matériau composite flexible selon l'une quelconque des revendications précédentes, dans lequel ledit manchon (2) a une épaisseur dans la gamme comprise entre 10 et 200 µm.

6. Matériau composite flexible selon l'une quelconque des revendications précédentes, dans lequel ledit manchon (2) est en contact étroit avec toute la périphérie dudit noyau (1).

7. Matériau composite flexible selon l'une quelconque des revendications précédentes, et comportant une multitude de parties comprimées annulaires espacées longitudinalement de la même distance les unes des autres sur la périphérie extérieure dudit manchon (2), chaque partie comprimée annulaire étant formée en comprimant à chaud dans la direction radiale de l'intérieur la périphérie du manchon (2) de manière à serrer ensemble le manchon et les fibres (3, 4).

8. Matériau composite flexible selon l'une quelconque des revendications précédentes, dans lequel lesdites fibres d'armement sont choisies parmi : fibres de carbone, fibres de verre, fibres de polyamide et leurs mélanges.

9. Procédé pour préparer un matériau composite flexible, comprenant les étapes consistant à :
   (a) fournir des fibres (3) en résine thermoplastique et des fibres d'armement (4), lesdites fibres (3) en résine thermoplastique fondant à une température à laquelle lesdites fibres d'armement (4) restent solides, et ayant un denier non supérieur à 3;
   (b) mélanger intimement lesdites fibres (3) en résine thermoplastique et les fibres d'armement (4);
   (c) assembler lesdites fibres mélangées afin d'obtenir un noyau (1); et
   (d) extruder une résine thermoplastique sur ledit noyau (1) pour former un manchon (2) entourant ledit noyau (1).

10. Procédé selon la revendication 9, dans lequel ladite étape de mélange (b) est exécutée tout en appliquant une traction d'au moins environ 2 g à chacune desdites fibres (3) en résine thermoplastique et desdites fibres d'armement (4).

11. Procédé selon la revendication 9 ou la revendication 10, comprenant en outre le traitement desdites fibres d'armement (4) avec un agent d'encollage avant ladite étape d'extrusion (b).

12. Procédé selon l'une quelconque des revendications 9 à 11, comprenant en outre le traitement dudit noyau (1) avec un agent d'encollage avant ladite étape d'extrusion (d).

13. Procédé selon l'une quelconque des revendications 9 à 12, dans lequel ladite étape d'extrusion (d) est exécutée tout en maintenant ledit noyau (1) sous vide de manière à sensiblement réduire les interstices entre les fibres mélangées (3, 4) dudit noyau (1) et entre ledit noyau (1) et ledit manchon (2).

14. Procédé selon l'une quelconque des revendications 9 à 13, comprenant en outre la compression à chaud dans le sens radial de l'intérieur du manchon (2) après ladite étape d'extrusion (d) de manière à former une multitude de parties en creux annulaires, espacées axialement de la même distance les unes des autres, sur la périphérie du manchon (2) de façon que les fibres mélangées (3, 4) et le manchon (2) soient étroitement liés au droit de chaque partie en creux.

15. Procédé selon la revendication 14, comprenant en outre la découpe en morceaux du produit obtenu après ladite étape de compression à chaud à des positions autres que les parties en creux.

Patentansprüche

1. Biegsames Verbundmaterial, das einen Kern (1), welcher im wesentlichen aus einer gleichförmig verteilten Mischung aus thermoplastischen Harzfasern (3) und Aussteifungsfasern (4) zusammengesetzt ist, und eine biegsame Hülse (2) umfaßt, welche aus einem thermopla-

stischen Harz besteht und den Kern (1) ummantelt, wobei die thermoplastischen Harzfasern (3) bei einer Temperatur schmelzen, bei der die Aussteifungsfasern (4) fest bleiben und eine Denier-Zahl nicht größer als 3 haben.

2. Biegsames Verbundmaterial nach Anspruch 1, worin die Mischung 15-30 Volumenprozent thermoplastische Harzfasern (3) und korrespondierend dazu 85-70 Volumenprozent Aussteifungsfasern (4) umfaßt.

3. Biegsames Verbundmaterial nach Anspruch 1 oder 2, worin die thermoplastischen Harzfasern (3) eine Faser-Denier-Zahl nicht größer als 1 haben.

4. Biegsames Verbundmaterial nach Anspruch 3, worin die Aussteifungsfasern (4) eine Faser-Denier-Zahl im Bereich von 0.25 bis 1 haben.

5. Biegsames Verbundmaterial nach einem der vorhergehenden Ansprüche, worin die Hülse (2) eine Dicke im Bereich von 10 bis 200 µm hat.

6. Biegsames Verbundmaterial nach einem der vorhergehenden Ansprüche, worin die Hülse (2) eng an die ganze Außenfläche des Kerns (1) angeschmiegt ist.

7. Biegsames Verbundmaterial nach einem der vorhergehenden Ansprüche und ausgestattet mit einer Vielzahl von longitudinal gleich auseinanderliegenden ringförmig gepreßten Bereichen auf der äußeren Außenfläche der Hülse (2), wobei jeder ringförmig gepreßte Bereich durch eine radial einwärts gerichtete Heißpressung der Außenfläche der Hülse (2) gebildet wird, um die Hülse und die Fasern (3,4) eng miteinander zu verbinden.

8. Biegsames Verbundmaterial nach einem der vorhergehenden Ansprüche, worin die Aussteifungsfasern aus Kohlefasern, Glasfasern, Polyamidfasern und Mischungen daraus ausgewählt werden.

9. Verfahren zur Herstellung biegsamer Verbundmaterialien mit folgenden Schritten:
(a) Verwendung von thermoplastischen Harzfasern (3) und Aussteifungsfasern (4), wobei die thermoplastischen Harzfasern (3) bei einer Temperatur schmelzen, bei der die Aussteifungsfasern (4) fest bleiben und eine Denier-Zahl nicht größer als 3 haben;
(b) enge Mischung von thermoplastischen Harzfasern (3) und Aussteifungsfasern (4);
(c) Zusammensetzung der gemischten Fasern, um einen Kern (1) zu erhalten; und
(d) Pressung eines thermoplastischen Harzes über den Kern (1) um eine Hülse (2) zur Ummantelung des Kerns (1) zu bilden.

10. Verfahren nach Anspruch 9, worin der Mischungsschritt (b) ausgeführt wird, während eine Spannung von mindestens 2 g auf jede der thermoplastischen Harzfasern (3) und Aussteifungsfasern (4) aufgebracht wird.

11. Verfahren nach Anspruch 9 oder 10, welches weiterhin umfaßt, daß die Aussteifungsfasern (4) vor dem Mischungsschritt (b) mit einem Klebemittel behandelt werden.

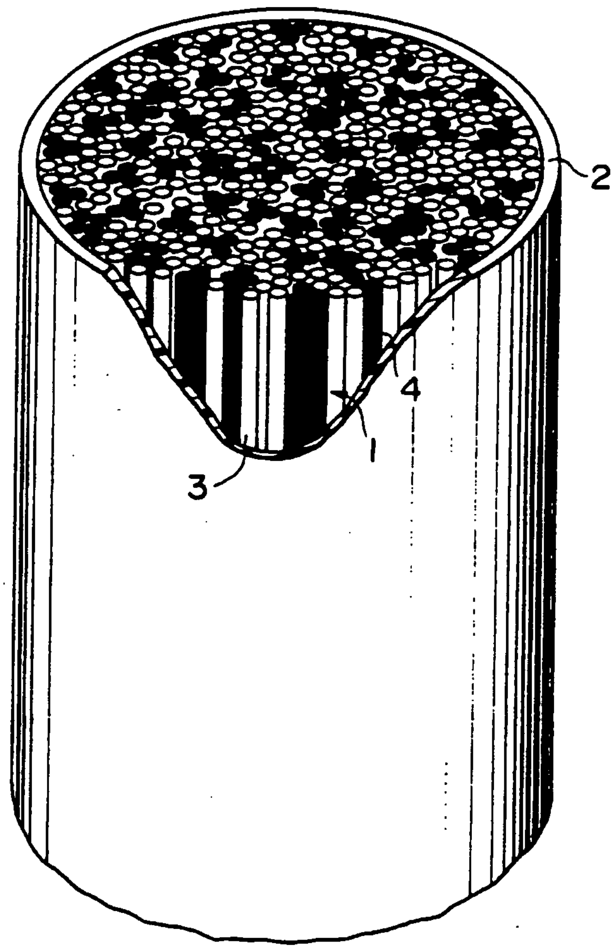
12. Verfahren nach einem der Ansprüche 9 bis 11, welches weiterhin umfaßt, daß der Kern (1) vor dem Schritt der Pressung (d) mit einem Klebemittel behandelt wird.

13. Verfahren nach einem der Ansprüche 9 bis 12, worin der Schritt der Pressung (d) ausgeführt wird, während dar Kern (1) unter Vakuum gehalten wird, so daß die Lücken zwischen den gemischten Fasern (3,4) des Kerns (1) und zwischen dem Kern (1) und der Hülle (2) im wesentlichen reduziert werden.

14. Verfahren nach einem der Ansprüche 9 bis 13, welches weiterhin umfaßt, daß die Hülle (2) nach dem Schritt der Pressung (d) radial einwärts gerichtet heißgepreßt wird, um eine Vielzahl von axial gleich auseinanderliegenden ringförmig gepreßten Bereichen auf der äußeren Außenfläche der Hülse (2) zu bilden, so daß die gemischten Fasern (3,4) und die Hülle (2) eng an jedem gepreßten Bereich begrenzt sind.

15. Verfahren nach Anspruch 14, welches weiterhin umfaßt, daß das Produkt, welches nach dem Schritt der Heißpressung erhalten wird, an anderen Stellen als den gepreßten Bereichen in Stücke geschnitten wird.

FIG. 1



F I G. 2